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Short communication

Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste

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ABSTRACT

Glycolysis of poly (ethylene terephthalate) bottle waste was carried out using microwave energy. A domestic microwave oven of 800 W was used with suitable modification for carrying out the reaction under reflux. The catalysts used for the depolymerization in ethylene glycol (EG) were zinc acetate and some simple laboratory chemicals such as sodium carbonate, sodium bicarbonate and barium hydroxide. Comparison of results was made from the point of view of the yield of bis (2-hydroxyethylene) terephthalate (BHET) and the time taken for depolymerization. It was observed that under identical conditions of catalyst concentration and PET:EG ratio, the yield of BHET was nearly same as that obtained earlier by conventional electric heating. However, the time taken for completion of reaction was reduced drastically from 8 h to 35 min. This has led to substantial saving in energy.

1. Introduction

Poly (ethylene terephthalate) (PET) finds use in a large number of utilities among which the fibers and disposable soft drink bottles predominate. Substantial solid waste generation coupled with high resistance to degradative assimilation into the environment makes it to be seen as a noxious material that demands its effective recycling [1].

Two main sources for PET recycling are the manufacturing waste and the post consumer waste [2]. Chemical recycling through depolymerization leads to the formation of materials which can react to form the polymer itself or some other secondary value added products [3]. Hydrolysis, aminolysis, methanolysis and glycolysis [4] are the routes to PET depolymerization, of which glycolysis and methanolysis have reached commercial maturity [1]. Glycolysis using ethylene glycol [5–10], diethylene and dipropylene glycol [8] and propylene glycol [11] results in the formation of oligomers or oligoester diols/polyols with hydroxyl terminal groups [5].

Microwave-assisted organic synthesis (MAOS), a new technique that has revolutionized synthesis moved to the forefront of chemical research [12,13]. Heating the material by microwave irradiation offers a number of advantages over the conventional heating, such as noncontact, instantaneous and rapid heating with high specificity. These characteristics have made it a popular technique for heating and drying materials and it is utilized in many households and industrial applications [13,14].

Microwave irradiation has been used for hydroglycolysis of PET pallets to reduce reaction time to less than 10 min in comparison with about 30 min at 100 °C heating in presence of various alcohols and alkalis. [15] The microwaves couple directly with the molecules those are present in a reaction mixture, leading to rapid but controllable rise in the temperature. Two fundamental mechanisms for transferring energy from microwaves to the substance being heated are the dipole rotation and the ionic conduction. Dipole rotation is an interaction between polar molecules, which try to align themselves with the rapidly changing electric field of the microwaves, resulting in transfer of energy. It is related to polarity of the molecules and their ability to align with the electric field. Ionic

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conduction results if there are free ions or ionic species present in the substance, which try to orient themselves to the rapidly changing electric field, generating ionic motion [16].

Hydrolytic depolymerization of PET in closed system under microwave irradiation with 2 MPa pressure and 90–120 min reaction time led to terephthalic acid, ethylene glycol and diethylene glycol as degradation products [17]. Similar studies were carried out by Zhang [18] using pure water at 220–230 °C at 2.0–2.5 MPa for 120–60 min. Krzan [19–21] during solvolysis in presence of zinc acetate catalyst and by using microwave (500 W) in a closed system achieved complete PET solubilization in about 5–10 min with methanol, diethylene glycol, propylene glycol and polypropylene glycol.

In the present study, we have attempted the use of microwave irradiation for PET glycolysis in EG under reflux conditions in place of conventional heating to obtain virtual monomer bis (2-hydroxyethylene) terephthalate (BHET). The catalysts used were zinc acetate, sodium carbonate, sodium bicarbonate and barium hydroxide of which the first three have been used in earlier glycolysis experiments using conventional heating source [9,10].

The results on the yield of BHET under these two sources of heating are compared through optimization of parameters (PET:EG ratio, catalyst concentration and time of glycolysis) for the yield of pure BHET.

2. Experimental

2.1. Materials

Discarded PET bottles were procured from local market. The bottles after removing caps and labels were cleaned by boiling in a weak detergent solution followed by washing and drying.

2.2. Chemicals

All the chemicals including the catalysts zinc acetate, sodium bicarbonate, sodium carbonate and barium hydroxide were of analytical reagent grade.

2.3. Glycolysis of polyester waste

A 700 W Electrolux (17L) domestic microwave oven was used at maximum power for the glycolysis reaction. A hole was made in the back panel of the oven to allow fitting of a condenser (Fig. 1). PET waste was treated with ethylene glycol using different PET:EG molar ratios (1:4 to 1:10) under reflux using microwave oven for time periods up to 60 min. The catalysts used were zinc acetate, sodium bicarbonate, sodium carbonate and barium hydroxide and their concentration was varied between 0.3% and 1% (w/w) in the reaction mixture. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation. The glycolyzed product was obtained as a residue after filtration. The filtrate contained unreacted ethylene glycol, bis (2-hydroxyethylene) terephthalate (BHET) and little quantities of a few water soluble oligomer. White crystals of BHET were obtained by first concentrating the filtrate by boiling and then chilling it. The glycolyzed residue was then boiled with water to extract any BHET left. White crystalline powder of BHET was purified by repeated crystallization from water, dried in an oven at 80 °C and weighed for estimating the yield. It was subjected to different characterization techniques, such as FTIR, NMR, and DSC.

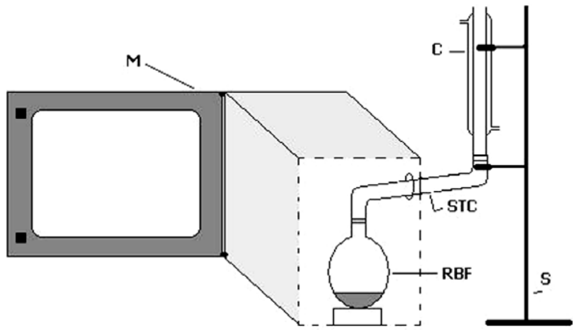

Fig. 1. Microwave reaction assembly.

2.4. Characterization of BHET

Melting point of the purified monomer, BHET was determined in an open capillary. Elemental analysis was carried out by using Heraus Combustion Apparatus. For ^{1}H NMR, the glycolyzed residue was dissolved in solvent $CDCl_3$. Tetramethyl silane was used as an internal standard and the spectrograph was recorded on JEOL, FT-NMR (60 MHz). FTIR spectrum was recorded using KBr disc technique on Shimadzu IR Spectrophotometer (Model 8400S). The melting characteristic was determined by differential scanning calorimeter (DSC) (Shimadzu 60) at the heating rate of 10 °C/min from 20 to 200 °C in nitrogen atmosphere.

3. Results and discussion

Earlier, we have reported that simple nontoxic chemicals like sodium carbonate, sodium bicarbonate, glacial acetic acid, lithium hydroxide, sodium sulfate and potassium sulfate can be used for PET glycolysis as catalyst in place of the conventionally used heavy metal catalysts zinc acetate and lead acetate. The experiments were conducted under reflux in EG using conventional electrical heating [9,10]. The products of glycolysis were BHET along with oligomers to a lesser extent, out of which BHET was separated by repeated crystallization. In the present communication, the study of ecofriendly glycolysis has been extended to the use of unconventional heating source of microwave radiations. The catalysts selected for this purpose were the conventional zinc acetate, sodium carbonate, sodium bicarbonate and barium hydroxide.

The glycolysis led to soluble BHET and insoluble residue of different oligomers. After filtration and repeated crystallization, pure BHET yield was measured. Each experiment was conducted three times and the average reading is reported. The glycolysis under microwave irradiation was optimized for maximum yield of BHET with respect to the time of reaction (Fig. 2), catalyst concentration (Fig. 3) and PET:EG ratio (Fig. 4).

Fig 2 indicates that the yield of BHET increased till 35–40 min for all the catalysts at concentration 0.5% (w/w) and PET:EG ratio 1:6, registering a decrease thereafter. It has been shown earlier by Campanelli et al. [22] that glycolysis of PET is a reversible equilibrium reaction, the reverse reaction being polycondensation. In the initial stages of depolymerization, polycondensation proceeds at extremely low rate and hence it can be ignored. With increase in time, this reverse reaction starts predominating thereby decreasing the BHET yield. To confirm repolymerization of BHET, it was treated in presence of EG and a catalyst (sodium carbonate) for a period of 20 min under microwave and TLC analysis of product was carried out using chloroform:ethanol; 90:10 as eluent. The TLC plate clearly indicated three spots, lower one corresponding to BHET and the higher ones corresponding to higher linear oligomers. These results have been established earlier by Campanelli et al. [22]. Thirty five

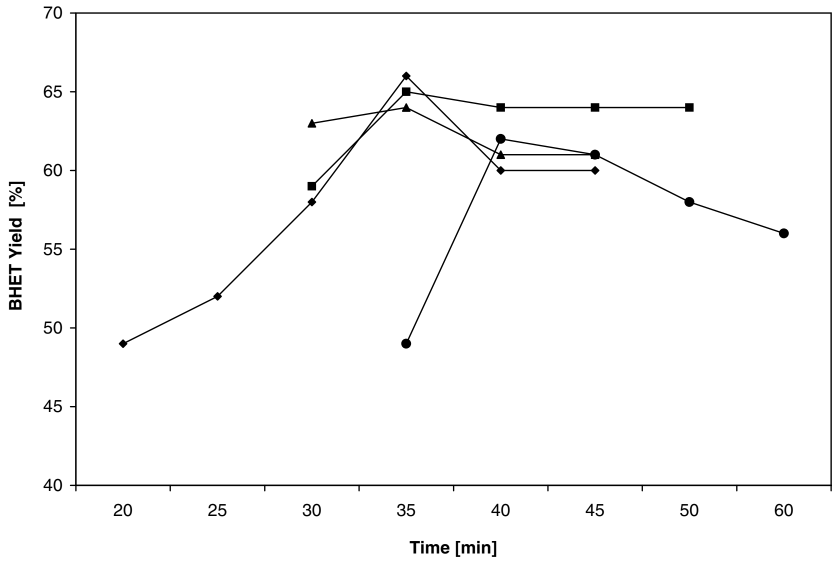

Fig. 2. Effect of glycolysis time on BHET yield. Catalyst concentration: 5% w/w, PET:EG: 1:6, zinc acetate (⧫), sodium carbonate (▲), sodium bicarbonate (■), barium hydroxide (●).

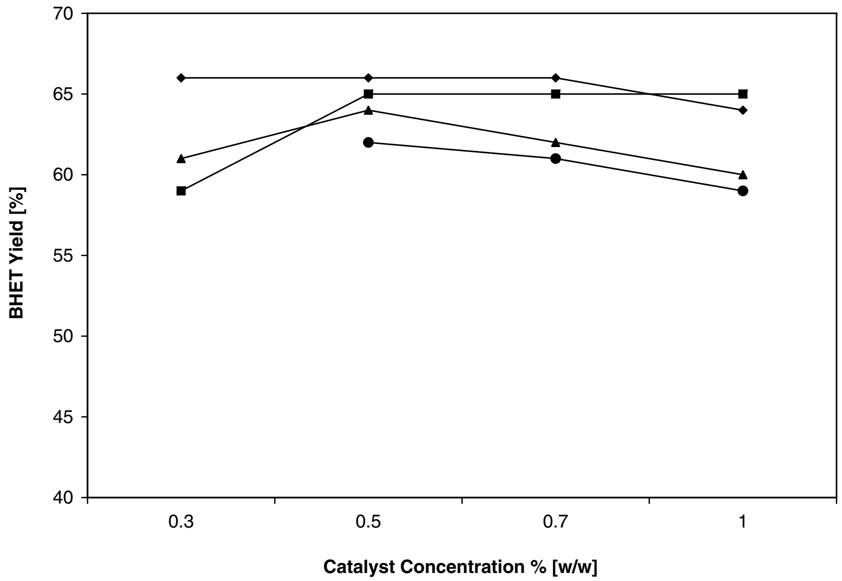

Fig. 3. Effect of catalyst concentration on BHET yield, time: 35 min (40 min for catalyst barium hydroxide), PET:EG: 1:6, zinc acetate (⧫), sodium carbonate (▲), sodium bicarbonate (■), barium hydroxide (●).

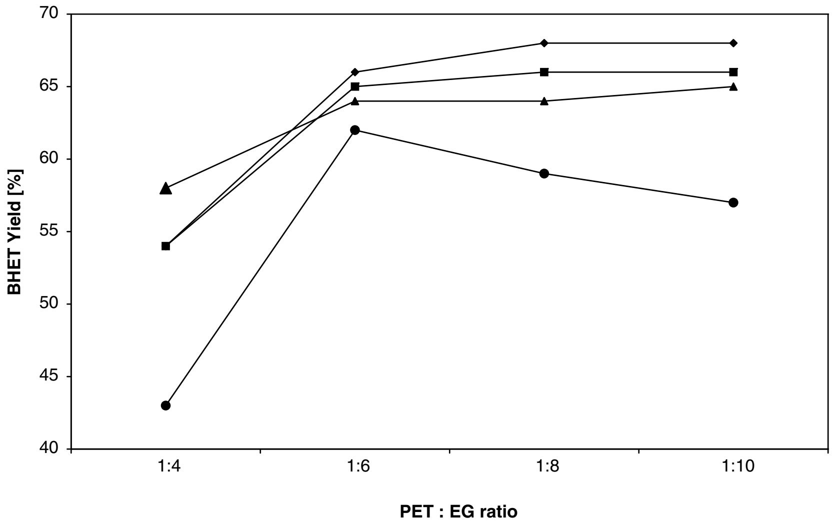

Fig. 4. Effect of PET:EG ratio on BHET yield, time: 35 min (40 min for catalyst barium hydroxide), catalyst concentration: 0.5% w/w, zinc acetate (♦), sodium carbonate (▲), sodium bicarbonate (■), barium hydroxide (●).

minutes was the time required in the case of zinc acetate, sodium bicarbonate and sodium carbonate catalysts while for barium hydroxide it was a little higher, 40 min. Thus, a decrease in the time of depolymerization reaction from 8 h to 35–40 min was observed on using microwave irradiation as a heating source for refluxing the reaction mixture. This may be attributed to the fact that microwaves do not affect the activation energy of the reaction but provides the momentum to the reactant molecules to overcome the barrier to reach the higher state helping in completion of reaction at a faster rate than by the conventional electric heating that employs conduction and convection of heat energy, first to the surface of reactants and then penetrating the reaction mass slowly. With this optimum time, optimization of catalyst concentration was carried out in the range of 0.3–1% (w/w) (Fig. 3). In all the cases, 0.5% (w/w) catalyst was sufficient to give maximum yield of BHET with PET:EG ratio 1:6 and time 35 or 40 min as optimized for different catalysts. Glycolysis is always carried out in excess of ethylene glycol [23] and hence the PET:EG ratio was varied from 1:4 to 1:10 and that required for obtaining maximum yield of BHET was found to be 1:6 in all the cases as observed from Fig. 4.

BHET, purified by repeated crystallization was subjected to TLC using the eluent chloroform:ethanol (9:1) wherein a single spot was obtained indicating the purity. The characterization by elemental analysis and melting point confirmed that the purified product of PET depolymerization

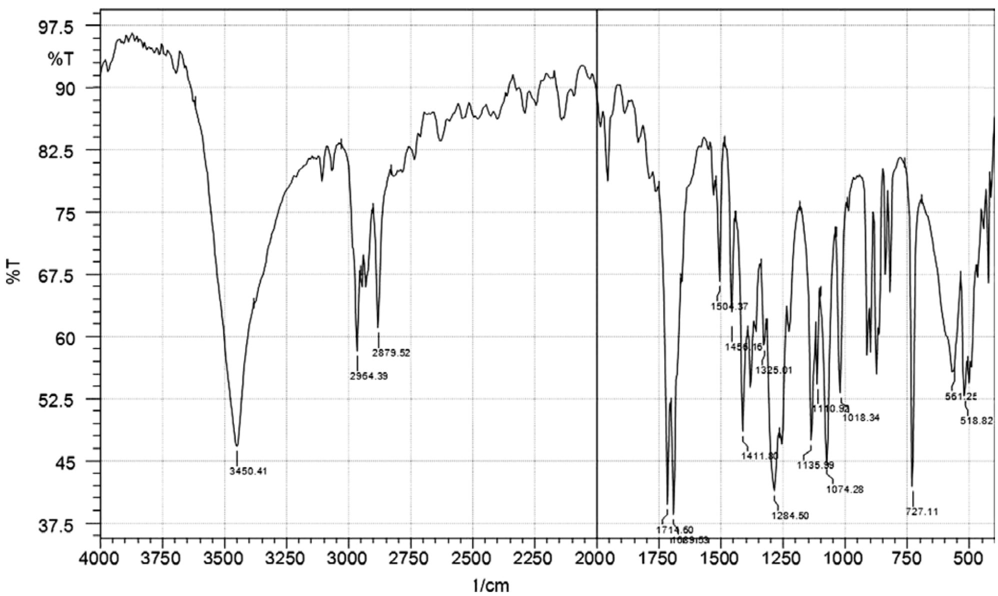

Fig. 5. FTIR spectra of BHET.

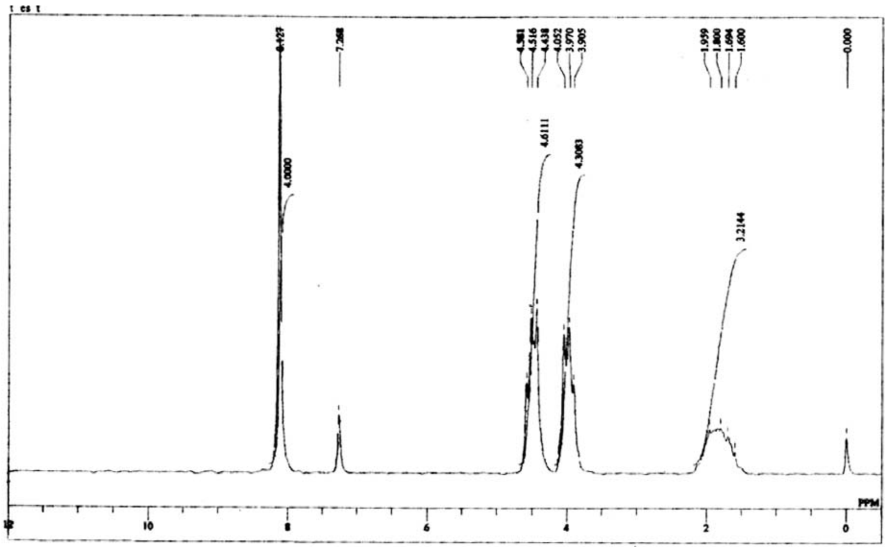

Fig. 6. NMR spectra of BHET.

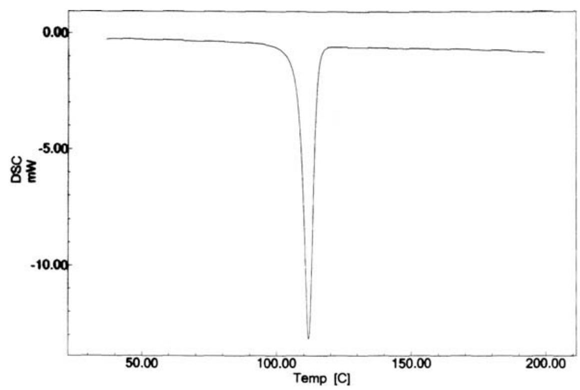

Fig. 7. DSC of BHET.

is BHET. The FTIR spectrograph (Fig. 5) of the purified monomer clearly showed –OH band at 3450 cm^{-1} and 1135 cm^{-1}, C=O stretching at 1715 cm^{-1}, alkyl C–H at 2879 and 2954 cm^{-1} and aromatic C–H at 1411–1504 cm^{-1}, present in BHET. The ^{1}H NMR (Fig. 6) gave peak at δ 1.9 corresponding to –OH groups, δ 3.99 corresponding to aliphatic $(–CH_2)_a$ proton, δ 4.51 corrosponding to aliphatic $(–CH_2)_b$ proton, and δ 8.1 corresponding to aromatic ring protons. The DSC scan (Fig. 7) also showed reasonably sharp endothermic peak at 109 °C in agreement with the known melting point of BHET [24].

The BHET yield obtained using microwave heating varied between a small margin on optimization of the reaction time, catalyst concentration and the PET:EG ratio. Thus, among the catalysts used, the lowest yield of BHET was obtained using barium hydroxide that too with extra 5 min of

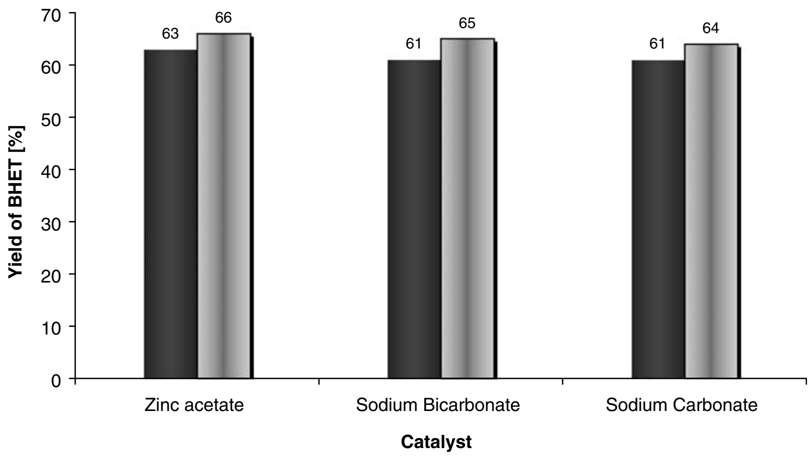

Fig. 8. Comparitive yield of BHET using different heating sources. Catalyst concentration: 0.5% w/w, PET:EG: 1:6, time: 8 h for conventional heating and 35 min for microwave heating. Conventional heating (■), microwave heating (■).

reaction. The maximum yield, (66%) although achieved by the heavy metal catalyst zinc acetate, was closely followed by sodium bicarbonate (65%) with 35 min reaction time.

When the results of microwave assisted depolymerization were compared with those achieved by conventional heating, in terms of BHET yield, (Fig. 8), the former proved to be better giving a little enhancement in the BHET yield. This gain is in addition to the saving in time of reaction with identical catalyst concentration and the PET:EG ratio.

4. Conclusions

Microwave irradiation was highly effective in completing the depolymerization reaction of PET waste. The use of microwave offers extremely short reaction time as compared to the conventional heating without adversely affecting the BHET yield, at the same time allows substantial energy conservation. Ecofriendly catalysts can be used in place of heavy metal catalyst such as zinc acetate. Thus the process attempted gives an ecofriendly alternative over the conventional glycolytic depolymerization with shorter reaction times.

Acknowledgment

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